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EVALUATION OF CERIUM OXIDE AS A LASER HOST

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THIRD QUARTERLY REPORT ON THE GROWTH AND EVALUATION OF CeO_2 AND ThO_2

During the third quarter investigation of the properties and crystal growth of ThO_2 was begun. Some work continued on attempts to grow large crystals of CeO_2 by slow cooling of the flux and by the gradient technique.

CRYSTAL GROWTH

ThO_2

It was found that ThO_2 was stable in the same fluxes and exhibited the same morphology changes as CeO_2. However, the solubilities were quite different as was the reaction with the flux medium. The solubility in $NaBO_2$ was very low compared with CeO_2 but about equal in PbF_2. There was also much less tendency for color center formation than with CeO_2 as determined by trans-mission spectra and visual examination. These were very weak with Ca^{2+} additions and non-existent with F^{-1} additions. Experiments were conducted with fluxes in the ternary system $NaF \cdot B_2O_3 \cdot PbF_2$. It was found that additions of NaF produced a great enhancement of solubility and crystal yield and had a lower vapor pressure than PbF_2-B_2O_3 alone. Using a flux composition of 75 Mole % PbF_2, 16.7 Mole % NaF and 8.3 Mole % B_2O_3, ThO_2 crystals have been

grown 4 x 4 x 3mm. These crystals grow as cubes and exhibit lamellar growth and flux inclusion like CeO_2, however, this is apparently very growth rate dependent because the latter growth, which occurs very slowly, is of very high quality growth. Frequently crystals are found with no growth defects and flux inclusion. It is expected that further reduction of growth rates will yield large crystals which are completely free of flux inclusions.

CeO_2

Several large slow cooling runs were made on CeO_2 using the $NaBO_2$ flux. One was at 0.25°/hour from 1300°C to 950°C. The quality and size of crystals obtained from this run were poor. The largest crystal was on the order of $3mm^3$. This melt lost 30% of its volume during the run by evaporation. It is believed that Na_2O is lost preferentially during prolonged heating. This results in a shift of the composition toward or into the region for cubic growth. Subsequent growth is of poor optical quality. CeO_2 was grown from PbO and PbF_2 with very low calcium content (7 ppm). The resulting crystals were yellow in color indicating color center formation due to this Ca^{2+} or possibly to Pb^{2+} in the crystal. Since the $NaBO_2$ and lead fluxes have shown serious drawbacks, the present emphasis is on the use of $Li_2Mo_2O_7$ as a

flux. This shows no deterioration in long runs, yields octahedra and yields colorless crystals.

A continued effort has been under way to grow CeO_2 by the gradient technique. High quality growth in excess of 0.02" per day has been achieved. Crystals 2 x 2 x 1mm have been grown by self seeding on a wire.

PROPERTIES

Visible emission has been observed in ThO_2 doped with Eu^{3+}, Sm^{3+}, Er^{3+}, Tb^{3+}, Pr^{3+} and Dy^{3+}. Ultraviolet emission from Gd^{3+} and infrared emission from Nd^{3+} has been observed. The position of the emission lines are typical for these rare earths. The lines are as narrow as those observed in CeO_2. Europium is particularly interesting having a strong narrow line (<1.5Å wide) at 7040Å which terminates 3000 cm^{-1} above the ground state. Eu^{3+} is easily excited in ThO_2 by UV or blue excitation even at low concentrations where as it is very weakly excited in CeO_2. This is mainly due to a shift of the absorption edge to higher energy. Energy transfer has been observed from Tb^{3+} or Eu^{3+} in ThO_2. No change has been noted in the emission linewidth of Eu^{3+} when Tb^{3+} is present up to 5%, although the brightness increased.

The usual objection to the use of ThO_2 as a laser is possible degradation of its optical properties due to its inherent radio-

activity. We have done radiation damage experiments which have led us to conclude that optical damage anneals out at a faster rate than it can occur and that other effects such as transmutation are unlikely because of the energy of the radiation involved.

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